

The fate of fuel-nitrogen during gasification of biomass in a pressurised fluidised bed gasifier

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Abstract

The distribution of fuel-nitrogen in gases, tar and char from gasification of biomass in a pressurised fluidised bed gasifier was investigated. Four species of biomass: birch, Salix, Miscanthus and Reed canary grass were gasified at 0.4 MPa and 900 °C. Oxygen-enriched nitrogen was used as fluidising agent. As a reference, gasification of Daw Mill coal was also carried out under the same experimental conditions. The experimental results illustrate that both the nature of the original fuels and the chemical structure of the nitrogen in the fuel have influence on the distribution of fuel-nitrogen in gases (NH₃, HCN, NO), tar and char under the employed experimental conditions. The present work also shows that the types of nitrogen heterocyclic compounds (NHCs) in the tar from different kinds of biomass are the same and the major compound is pyridine. However, the distribution of the various NHCs in the tar from the four species of biomass varies: the higher the content of fuel-nitrogen, the higher the concentration of two-ring NHCs in the tar. An effective method for extracting NHCs from the acidic absorption of the product gas was introduced in the present work. The method makes use of solid phase extraction (SPE) by a silica-based C₁₈ tube to extract the NHCs which subsequently were analysed by gas chromatography (GC) with flame ionisation detection (FID). The recovery and reproducibility of the SPE technique for NHCs is discussed. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Gasification; Biomass; Nitrogen compounds

1. Introduction

Currently, biomass accounts for 14–15% of worldwide energy consumption. The biomass combustion process yields heat, which is used to fulfil basic energy requirements for homes and various industries in developing countries [1]. The biomass energy plantation and conversion systems are an effective source of renewable energy and have had a substantial impact on reducing the global CO₂ emission budget [2]. Since energy from biomass is an effective substitute for fossil fuels, it has also been widely used in devel-

oped countries over the last century [3]. In recent years, the decreasing availability of fossil fuels has become a growing concern and using fossil fuels is faced with stricter environmental regulations [4]. Therefore, a much greater interest in the use of biomass energy as an alternative to fossil fuels has developed. Among the biomass thermochemical conversion processes, pyrolysis, gasification and combustion, biomass gasification should be explored further since biomass gasification can form a solid basis of new promising energy conversion technologies. Among these are fuel cells and integrated gasification combined cycle (IGCC) installations. Conditioning and upgrading the biomass gasification product gas can make it a suitable feed for methanol or Fischer–Tropsch liquid synthesis [5].

During solid fuel thermochemical conversion the fuel-nitrogen is converted to ammonia (NH₃), cyanide (HCN), isocyanic acid (HNCO), nitrogen oxides (NO_x and N₂O), molecular nitrogen (N₂) and organic nitrogen.

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¹ Dr. G-X. CHEN worked on all the gasification experiments and reviewed the paper. He passed away two years ago. This paper is dedicated to the memory of Dr. G-X. Chen for his contribution to the biomass thermochemical research field.

Part of the fuel-nitrogen remains in the char. NH_3 , HCN, H₂NCO and organic nitrogen in the product gas pass through end-use systems, where they can poison catalysts or fuel cell internals. It is well known that NH_3 , HCN, H₂NCO and organic nitrogen are the precursors to the emissions of nitrogen oxides (NO_x and N_2O). Nitrogen oxides are pollutants causing photochemical smog, acid rain, the greenhouse effect and ozone depletion [6]. Therefore an intensive study on the formation of the precursors of nitrogen oxides during fuel thermochemical conversion is going on in many countries. However, the mechanisms for the formation of the precursors of nitrogen oxides during thermochemical conversion processes of solid fuels are still not clear, especially in the case of biofuels. The purpose of the present work is to investigate the correlation between the characteristics of the raw materials and the distribution of fuel-nitrogen in products (disregarding molecular nitrogen) under the studied experimental conditions. Two cultivated energy crops, Reed canary grass and Miscanthus, and a fast growing energy forest specie, Salix, as well as birch wood were employed. Daw Mill coal of UK origin was used as a reference. The factors influencing fuel-nitrogen conversion to the gases (HCN, NH_3 , NO) or retention in the char as well as the distribution of individual NHCs in the tar are discussed in brief. A solid phase extraction (SPE) method for extracting the NHCs from the acidic absorption of the product gas was established and is presented.

2. Experimental

2.1. Materials

The feedstocks used were four species of biomass (1–3 mm, ~5.3% moisture): birch, Salix, Miscanthus, Reed canary grass, and Daw Mill coal of UK origin (1–1.35 mm, 7.3% moisture). The chemical composition of the fuels is listed in Table 1.

The sample source was a pressurised fluidised bed reactor (silver sand as bed material) operated at 900 °C and 0.4 MPa. Oxygen-enriched nitrogen was used as fluidising agent. The concentration of oxygen in the fluidising agent controlled the temperature of the bed in the experiments [7,8]. The solvent required for sample preparation, chemi-

cals for preparation of calibration standards and internal standards were used as received, i.e. at a minimum purity of 98–99% (Sigma–Aldrich, Sweden). SPE ENVI-C₁₈ tubes (Supelco, Inc., Bellefonte, US) required for sample preparation were loaded with 500 mg of octadecyl-bonded end-capped silica (surface area 400–600 m² g⁻¹, average particle size 50–60 μm and average pore diameter 60–70 Å).

2.2. Sampling

Fig. 1 shows the sampling system for gaseous and liquid nitrogen compounds. The first two traps containing 0.1 M H_2SO_4 (2 × 40 ml) were used for sampling of both NH_3 and NHCs. HCN was absorbed in the following four bottles of which two contained 0.1 M NaOH (2 × 50 ml in the second and the third bottle). The last four traps containing dichloromethane (DCM) were used to wash out the residual tar from the gas flow before the gas entered the volume measurement meter.

A stream of the product gas from the top of the gasifier passed through a bypass pipe, which was warmed up to about 250 °C, and bubbled through the sampling system. The gas volume measurement meter was placed at the end of the sampling system to record the total volume of sampled gas. The gas flow was controlled at about 5 l min⁻¹. The sampling time was about 1 h. A char sample was collected at the end of each experiment (about 1 h) after the temperature and the pressure in the gasifier had been reduced to room temperature and atmospheric pressure.

2.3. Sample preparation

The acidic solution in the first two impingers was extracted with a small portion of DCM in order to remove phenolic and neutral tar fractions. The water phase was poured into a funnel equipped with a folded filter paper. The filtrate was then transferred into a 100 ml volumetric bottle and brought to volume with 0.1 M H_2SO_4 .

A SPE method was used to remove any trace of organic compounds from the filtrate in order to protect the electrodes that were used for measuring ammonia. A SPE ENVI-C₁₈ tube was conditioned with a 1 ml methanol followed by three tube fillings of distilled water. A part of the

Table 1
The chemical composition (wt.%, db^a) of the fuels

Fuel	C	H	N	O	S	Ash	Fixed carbon	Volatiles	Heating value (MJ/kg,daf ^b)
Birch	49.0	6.1	0.1	44.5	<0.01	0.4	n.d. ^c	n.d.	19.3
Salix	48.1	6.2	0.4	43.9	0.036	1.6	14.9	82.6	19.2
Miscanthus	47.9	6.3	0.7	43.8	0.11	2.8	n.d.	78.5 ^d	17.0
Reed canary grass	44.2	6.0	0.8	41.7	0.21	8.8	n.d.	73.5 ^d	17.6
Daw Mill coal	73.8	4.9	1.3	12.3	1.63	6.5	58.5	35.6	30.4

^a db: dry basis.

^b daf: dry and ash free.

^c n.d.: not determined.

^d Source: Ref. [40].

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